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STUDY OF NICKEL HYDROXIDE ELECTRODES II
OXIDATION PRODUCTS OF NICKEL (II) HYDROXIDES

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Study of Nickel Hydroxide Electrodes II

Oxidation Products of Nickel (II) Hydroxides

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Includes 8 figures

Summary

The pure phases of some oxidized nickel hydroxides concerned with the nickel hydroxide electrode of an alkaline accumulator were prepared. The crystallographic data of these phases, their chemical behavior and conditions of transition were studied.

Introduction

In our first article¹ we reported on hydroxides of bi-valent nickel and on some conditions as they exist with high-valency nickels. The extent of the studies on higher nickel hydroxides has been fully outlined by Milner and Thomas². The present work describes some newly found compounds and submits a proposal for classifying nickel hydroxides.

Two structural configurations have been established for hydroxides of bi-valent nickel:

1. The hydroxide $\text{Ni}(\text{OH})_2$, named β -type, crystallizes in its brucite form. It is made of $\text{Ni}(\text{OH})_2$ layers in which oxygen ions form a hexagonal, dense spherical packing (the arrangement is hexagonal with $a = 3.12 \text{ \AA}$ and $c = 4.60 \text{ \AA}$; compare 4.1).

Author's list at end of translation

2. The hydroxide $3 \text{ Ni(OH)}_2 \times 2 \text{ H}_2\text{O}$, named δ -type, consists of chains of two oxygen ion layers each of which corresponds to the β -type but is separated by a layer of water molecules. This results in an enlargement of the elementary cell in the c-axis from 4.60 Å to 7.5 Å. The a-axis remains practically unchanged (compare 4.2)

The oxidation products $^{3-7}$ can also be arranged into two similar structural configurations:

1. The so-called $\beta\text{-NiO(OH)}^3$ compound is isotypical with the bi-valent $\beta\text{-Ni(OH)}_2$; the a-axis is decreased from 3.12 Å to 2.81 Å during oxidation while the c-axis is lengthened from 4.60 Å to 4.76 Å and 9.53 Å. The x-ray diagram has less line density than the bi-valent hydroxide (4.3) since all (hkl) reflexes disappear during oxidation.

2. The products named Y-hydroxides³ can be indexed in either a hexagonal or monoclinic manner. The hexagonal configuration results in a grid constant $a = 2.83 \text{ Å}$ and $c = 6.96 \text{ Å}$. The enlargement of the c-axis is due to an intermediate layer consisting of water molecules as well as alkali and hydroxide ions.

The substances of the y-phase occur with two modifications which can be distinguished by means of x-ray diagrams. These two structures are called the y , and y_2 phases (4.4, 4.5).

The following describes β -types such phases where the x-ray diagram can be indexed hexagonally with a c-axis of 4.6 to 4.8 Å or multiples thereof. The δ and y -types, on the other hand, show an enlarged c-axis of 7.0 to 7.5 Å due to the presence of an intermediate layer. The y-phases are characterized by the presence of sodium or potassium inside the grid. The distances between oxygen atoms for the reduced phase of the hydroxide layers (δ and β II phase) are 3.1 Å and 2.83 Å for the oxidized phase (y , y_2 and β III).

Experiment Section

1. Analytic Procedure

For the quantitative analysis nickel is determined by dimethylglyoxim and alkali by the flame-photometric method. The oxidation value is determined by the iodine-metric method. A small, random-weight sample, collected from a substance not yet fully dried, is used for iodine-metric determination of active oxygen. The nickel content is determined complexometrically. It is generally true that in a still slightly wet substance the oxidation value is somewhat higher than after the drying of same. Determination of water content is done by heating the substance together with potassium chromate to 1000°C and by absorption of water in calcium chloride. The pycnometric density is measured in absolute kerosene (K_p $150-200^{\circ}\text{C}$).

2. Methods for the production of high valency nickel hydroxide

2.1 Production based on sodium-niccolate (III)

Basic nickel carbonate (pure, Merck) is heated to 300°C for five hours. The resulting black nickel oxide is admixed with dry sodium-peroxide and sodium-hydroxide at weight proportions of 1:0.75:1.75 and fused together at 800°C in an oxygen atmosphere. After cooling ($\frac{1}{2}^{\circ}\text{C}$ per minute) and rinsing the pulverized melt with alcohol and ether, a large-grained powder of NaNiO_2 is obtained partially consisting of single crystals.

NaNiO_2 at room temperature decomposed in water under agitation and repeated decanting produces $\text{NiO}_{1.50} \times 0.77 \text{H}_2\text{O} \times 0.062 \text{Na}_2\text{O}$ after a hydrolyzing period of 30 hours.

A hydrolyzing period of 172 hours of the same substance still leaves 0.1 atom sodium per atom nickel. If 0.5 sodium lye solution is used instead of water then one obtains the reaction product $\text{NiO}_{1.48} \times 0.94 \text{H}_2\text{O} \times 0.060 \text{Na}_2\text{O}$.

X-ray diagrams show the presence of the γ -phase and the β (II) -phase (4.1 and 4.4).

When hydrolyzing NaNiO_2 with alkaline solutions and bromide, the mixture should be mixed with ample reagents, constantly stirred, while excluding carbon dioxide from the air. It is then decanted after several hours have elapsed. Repeating this procedure once or twice it is then exhausted in a G-4 frit, cleansed of alkali and bromide with ice water and dried over H_2SO_4 or P_4O_{10} . This produces a black to metallic-grey sheen and large-grained substance. It is not affected when stored under dry conditions.

The Debyeogram shows the sharp reflexes of the γ -phase (table 7). The oxidation values fluctuates between $\text{NiO}_{1.67}$ and $\text{NiO}_{1.83}$. The test data is shown in table 1.

During drying between $100\text{--}150^\circ\text{C}$ the product of phase γ gives off half of the still present water. Starting with $\text{NiO}_{1.79} \times 0.69 \text{ H}_2\text{O} \times 0.15 \text{ Na}_2\text{O}$ (γ_1 -phase) results in a product at 150°C composed of $\text{NiO}_{1.73} \times 0.36 \text{ H}_2\text{O} \times 0.16 \text{ Na}_2\text{O}$ with a high density line diagram.

A well-crystallized preparation of the γ_1 -phase (composition: $\text{NiO}_{1.81} \times 0.61 \text{ H}_2\text{O} \times 0.13 \text{ K}_2\text{O}$; nickel content = 53.4%) was used to determine the magnetic susceptibilities (Bronger⁸, compare table 2).

2.2 Production based on salts of nickel (II) with alkali solution and bromide

A solution of $25\text{g Ni}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ in 40 ml water is drip-fed - under exclusion of carbon dioxide - into 125 ml 2n alkali solution with 2-3 ml bromide at room temperature. The solution is stirred for two hours and then decanted. This oxidation must be repeated at least twice. The filtrated sediment is cleansed of bromide and alkali and dried over P_4O_{10} . The result is a dark-black, not well-crystallized product (table 3). The oxidation values are not very high. The powder diagrams are to be indexed according to the γ_2 -type (4.5) (table 8).

Incomplete and non-repeating precipitation with sodium hypobromide produces $\text{NiO}_{1.5} \times \text{H}_2\text{O}$ (to be read as $\text{NiOOH} \times \text{Ni}(\text{OH})_3$). The x-ray data indicates a superstructure of the β -phase with the c-axis doubled (4.3).

The Curie-Weiss law has been taken into account with a Curie-temperature of $\Theta = -25^{\circ}\text{K}$.

1) Ansatz	2) Analyse	3) Pyknometrische Dichte
30 g NaNiO_2 + $2 \times (11.6 \text{ n NaOH} + 6 \text{ ml Br}_2)$	$\text{NiO}_{1.82} \cdot 0.73 \text{ H}_2\text{O} \cdot 0.15 \text{ Na}_2\text{O}$	3,80
19 g NaNiO_2 + $3 \times (11.6 \text{ n KOH} + 4 \text{ ml Br}_2)$	$\text{NiO}_{1.81} \cdot 0.55 \text{ H}_2\text{O} \cdot 0.13 \text{ K}_2\text{O}$	3,78
1,5 g NaNiO_2 + 100 ml 0,5 n NaOH + 0,33 ml Br_2 (Dauer 84 h)	$\text{NiO}_{1.88} \cdot 0.76 \text{ H}_2\text{O} \cdot 0.10 \text{ Na}_2\text{O}$	

Table 1: Product from NaNiO_2

1) Initial preparation 2) analysis 3) pycnometric density

T °K	$\chi_{\text{Mol}} \cdot 10^4$	μ_B (BOHRsche Magnetonen)
90	1692	1,25
195	830	1,21
295	582	1,22

Table 2: Magnetic properties of the γ_1 -phase

Even repeated precipitation with bromide lithium hydroxide solution (2n) results in oxidation products which correspond to the β (III)-phase. A constant presence of Li^+ ions is quite clearly built into the oxygen level the same as with the nickel ions. Bromic rubidium and cesium hydroxide solutions produce practically alkali-free reaction products whose x-ray diagrams indicate a β (III)-phase (table 6). Analysis shows the formula $\text{Ni}(\text{OH})_3$. Assuming a hydrogillit structure ($\text{al}(\text{OH})_3$) this works out at an x-ray density of 3.72 g/cm^3 .

2.3 Oxidation of nickel hydroxides

2.3.1 With hypobromide. 2g β -nickel (II) hydroxide ($\text{NiO} \times 1.3 \text{ H}_2\text{O}$) (from 0.5 m nickel nitrate solution with 0.1 n potash lye at 80°C and drying the nitrate-free condensation over P_4O_{10}) are suspended in a small amount of 9 n lye and added to a hypobromide solution (100 ml 9 n sodium or potash lye plus 3 ml bromide). After stirring for one hour and subsequent settlement, the sediment is then filtrated and cleansed of alkali and bromide. The oxidation is repeated once.

Analysis: $\text{NiO}_{1.68} \times 0.52 \text{ H}_2\text{O} \times 0.102 \text{ K}_2\text{O}$ or $\text{NiO}_{1.73} \times 0.76 \text{ H}_2\text{O} \times 0.095 \text{ Na}_2\text{O}$. The substances generally possess the structure of the γ_2 -phase.

The oxidation of β -nickel (III) hydroxide corresponds to the above.

2.3.2. With peroxodisulfate. 0.7 g β -nickel (II)-hydroxide ($\text{NiO} \times 1.5 \text{ H}_2\text{O}$) are ground together with 3 g $\text{K}_2\text{S}_2\text{O}_8$, covered with 100 ml 1 n KOH and decanted after standing for several days. It is then filtrated and washed clear of peroxosulfate. Drying over P_4O_{10} results in substances of the β -phase with the composition of $\text{NiO}_{1.55} \times 1.0 \text{ H}_2\text{O}$ and $\text{NiO}_{1.42} \times 1.0 \text{ H}_2\text{O}$. The compound $\text{Ni}(\text{OH})_3 \times \text{NiOOH}$ and $2 \text{ NiO}(\text{OH}) \times \text{H}_2\text{O}$ results in an x-ray density of 4.20 g/cm^3 and density (pylen) of 4.35.

2.3.3. Oxidation of the nickel hydroxide. 1.5 g α -nickel hydroxide are admixed to a solution of hypobromide (consisting of

1) Ansatz	Phase	2) Analyse	3) Dichte (pykn.)
4) 25 g $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ + 40 ml Wasser tropfenweise unter Rühren in 125 ml 2 n KOH + 3 ml Brom (2× wiederholt bei Zimmertemperatur)	γ_2	$\text{NiO}_{1,66} \cdot 0,76 \text{H}_2\text{O} \cdot 0,079 \text{K}_2\text{O}$	
5) 25 g $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ + 50 ml Wasser in 125 ml 2 n KOH + 3 ml Brom (2× wiederholt bei Zimmertemperatur)	γ_2	$\text{NiO}_{1,62} \cdot 0,78 \text{H}_2\text{O} \cdot 0,074 \text{K}_2\text{O}$	
25 g $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ + 50 ml H_2O + 4× (200 ml 2 n LiOH + 6 ml Brom) - 6)	β (III)	$\text{NiO}_{1,59} \cdot 1,27 \text{H}_2\text{O} \cdot 0,045 \text{Li}_2\text{O}$	
12,5 g $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ + 25 ml H_2O + 90 ml 2 n NaOH + 3 ml Brom - 6)	β (III)	$\text{NiO}_{1,48} \cdot 1,10 \text{H}_2\text{O}$	d = 3,83
6,25 g $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ + 13 ml H_2O + 50 ml Rb(OH) + 1,5 ml Brom - 6) (RbOH = 1,77 n RbOH + 0,15 n Rb_2CO_3)	β (III)	$\text{NiO}_{1,50} \cdot 1,45 \text{H}_2\text{O}$	d = 3,98
12,5 g $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ + 25 ml H_2O + 90 ml 2 n CsOH + 3 ml Brom - 6)	β (III)	$\text{NiO}_{1,48} \cdot 1,24 \text{H}_2\text{O}$	d = 3,83

Table 3: Production from nickel (II) - saline solution

1) Initial compounds 2) analysis
 3) density (Pykn) 4) 25g $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$
 + 40 ml water, drip-fed under agitation into
 125 ml 2 n KOH + 3 ml bromide (repeated twice
 at room temperature 5) 25 g $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$
 + 50 ml water into 125 ml 2n KOH + 3 ml bromide
 (repeated twice at room temperature) 6) bromide

100 ml 0.5 n potash lye and 2 ml bromide) and stirred for three hours. After settlement and filtration it is cleansed with icewater of alkali and bromide and dried in a dessicator over P_{40} : Analysis: $\text{NiO}_{1,73} \cdot 0,55 \text{H}_2\text{O} \cdot 0,10 \text{K}_2\text{O}$; γ_2 -phase.

2.4 Electro-chemical oxidation

Thin layers of α -nickel hydroxide result after about 15 hours when a current of $0,04 \text{ mA/cm}^2$ is sent through 0.1 m nickel nitrate solution onto nickel sheets both surfaces of which are of 48 cm^2 . Such laboratory conditions produce about $0,7 \text{ mg/cm}^2$ well-adhering, crystalline α -nickel hydroxide. The layer thickness is about $2,6 \mu$. The α -nickel hydroxide can be changed completely to

β -nickel (II) hydroxide by placing it into 7 n KOH at 70°C for a few hours. It was not yet possible to obtain a direct, cathodic separation of β -nickel hydroxide.

Thin nickel hydroxide layers offer good electrical contacts with the carrier and can be quantitatively oxidized.

2.4.1 Galvanimetric oxidation of α -nickel hydroxide. Two electrodes with 0.1 mA/cm² in 0.1 KOH were connected anodically to determine capacity. The electrolyte concentrations were kept that low in order to avoid transformation of α into β nickel hydroxide.

Oxygen formation increases noticeably with increasing voltage. Discharging tests showed that when oxygen formation commences the oxidation of nickel hydroxide is complete. In order to follow the course of the oxidation, two electrodes at a time, with nickel hydroxide layers of 25, 52, 78 and 200%, were given the necessary current under the above conditions. Debyeograms were made of the oxidized products and the oxidation value were analytically determined.

2.4.2 The galvanimetric oxidation of β -nickel (II) hydroxide is the same as for α -nickel hydroxide. Since α and β nickel hydroxide must be oxidized differently, the voltage load quantity for complete oxidation must be determined separately.

Fig. 1 plots the analytically determined oxidation values for α and β -nickel hydroxide in relation to the applied current quantity (as a percentage of current quantity required to induce oxygen formation).

The oxidation shows a linear increase to 100% of applied current quantity. Continuing oxidation beyond the oxygen formation (at 100% load) produces only small increases in oxygen values. The oxidation value for completely oxidized α -nickel hydroxide is near NiO_{1.75} and for β -nickel hydroxide near NiO_{1.50}.

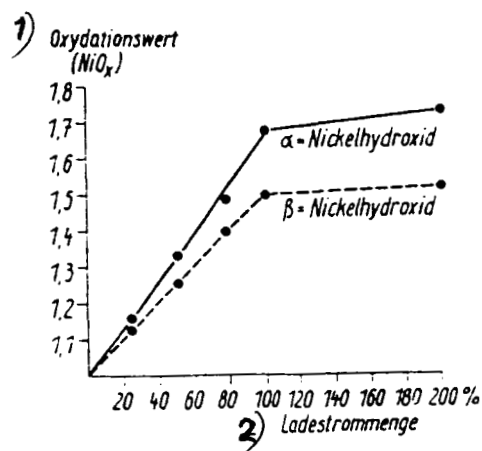


Fig. 1: Relationship between oxidation value and absorbed current quantity during galvanometric oxidation of α and β nickel hydroxide

1) oxidation value 2) electric current quantity

The results of x-ray photos are shown in form of line diagram in Fig. 2 with oxidation values and electric current as parameters. Fig. 3 shows the oxidation of β -nickel (II) hydroxide. The main lines are indexed.

Initial and final products have differing x-ray diagrams. α nickel hydroxide changes into the γ -phase, and β -nickel (II) hydroxide into β -nickel (III) hydroxide. Partially oxidized electrodes show mixtures of initial and final products.

2.4.3 Electro-static oxidation and reduction

An ample supply of electrodes as per 2.4 should be on hand so that a new electrode can be used for each current value. 0.1 n KOH is selected as electrolyte. The electrode potentials are calibrated against Hg/HgO reference electrodes (at a temperature of 25°C) but calculated for the water electrode in the same medium.

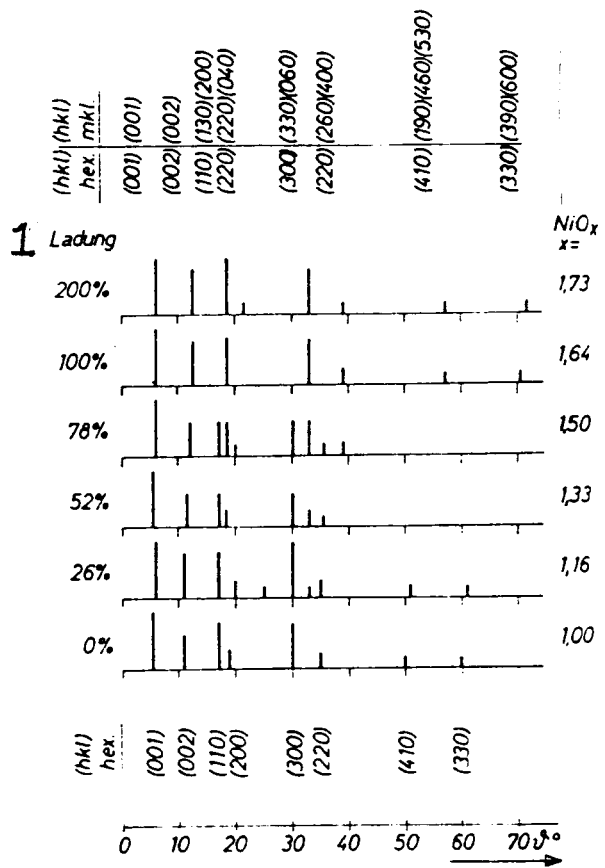


Fig. 2: Galvanimetric oxidation of α-nickel hydroxide
1) current load

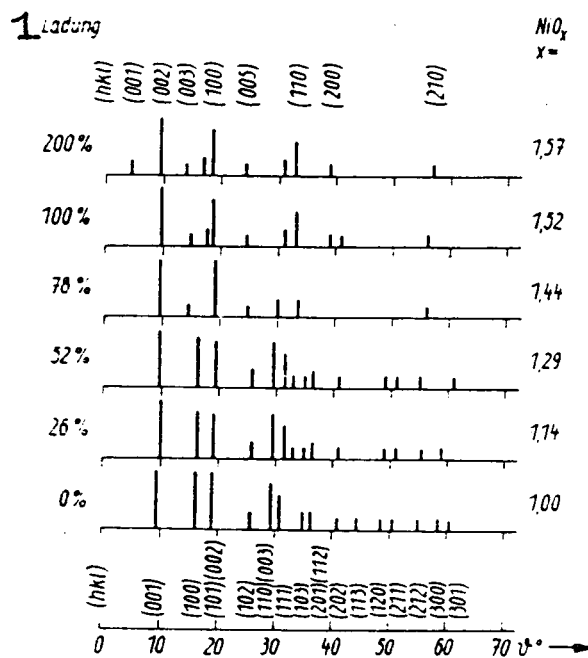


Fig. 3: Galvanimetric oxidation of β-nickel (II) hydroxide

Oxidation sets in immediately. Prior to reduction, the electrodes are initially completely oxidized (α-nickel hydroxide at 1420 mV and β-nickel hydroxide at 1470 mV). The reduction is considered complete when the electric current has slowed to a residual flow which under anodic load is always anodic and can

be considered as an equalization of self-discharge. During cathodic load the direction of the residual flow will be dependent on the potential. The flow will turn anodic once above the potential of about 1320 mV below which the residual flow will remain cathodic.

On completion of the reaction the oxidation value is determined and an x-ray-gram taken.

Fig. 4 and 5 show the oxidation values for the α and β -nickel hydroxides in relation to the voltage.

A noticeable oxidation for both initial substances occurs only above a certain potential. For α -nickel hydroxide it is about 1380 mV and for β -nickel hydroxide about 1430 mV. Complete oxidation above this threshold occurs only in a very narrow potential range.

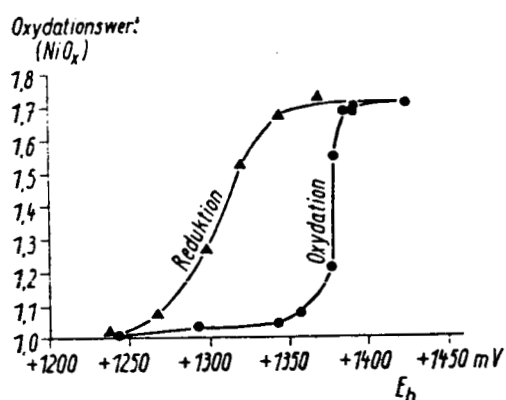


Fig. 4: Oxidation value of α -nickel hydroxide in relation to voltage

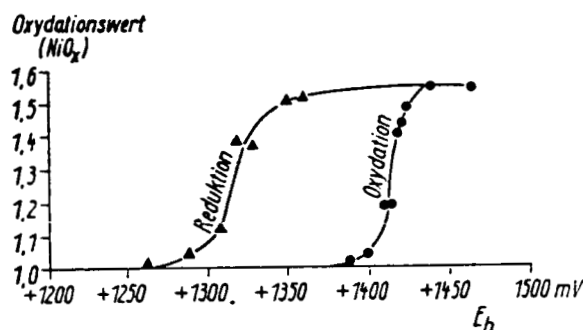


Fig. 5: Oxidation value of β -nickel hydroxide in relation to voltage

Noticeable reduction of the γ -substance does not take place below about 1320 mV. This value is more negative by about 60-70 mV than the required voltage for oxidation. Reduction also takes place in a narrow potential range. For reactions between β -nickel (II) hydroxide and β -nickel (III) hydroxide, the difference between oxidation and reduction potential is still more pronounced and amounts to about 100mV. Corresponding potential differences have been noted between galvanimetric oxidation and reaction.

Fig. 6 and 7 show the Debyeogram of the electro-static series of measurements giving the potential and the oxidation values. The narrow potential intervals, within which oxidation and reduction occur, can be clearly recognized.

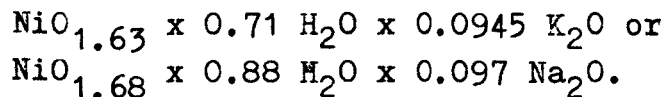
The (001)-reflexes are shifted monotonically with the oxidation value of $c = 7.5 \text{ \AA}$ during the α - γ -reaction. The reverse occurs for the cathode treatment. The (hko)-reflexes, referred to the hexagonal indicators, show the heterogenic course of the transformation. The intermediate levels of the oxidation values show double the lines for identical indicators, i.e., $a = 3.1 \text{ \AA}$ for the reduced and $a = 2.85 \text{ \AA}$ for the oxidized phase. This process is reversible.

While β -nickel (III) hydroxide oxidizes into β -nickel (III) hydroxide one can recognize a continuous course of the (001)-reflexes which corresponds to an enlargement of the c-axis from 4.6 \AA to 4.7 \AA . The (hk0)-reflexes for transitional products - as already noted for the α - γ reaction - occur as double formation. The (hkl)-reflexes of the β -nickel (II)-hydroxide disappear with increasing oxidation but reappear during reduction.

2.4.4 Electro-chemical oxidation of β -nickel (II) hydroxide. Chemically sedimented β -nickel (II) hydroxide will oxidize with 3% weight of water:

300 mg $\text{Ni}(\text{OH})_2$ is rubbed into the netting of two nickel grids of 40 x 40 mm. The grids are placed on top of each other and pressed onto a piece of nickel plate provided with a conductor.

The edges of the support plate are bent around the grids. Nickel counter-conductors are arranged above at about 2 cm distance. After loading the system anodically for about 40 hours with 5 mA in 9 n KOH or NaOH the following oxidation products results:



The x-ray diagrams correspond to the γ_2 -structure.

2.5 Production methods for the γ and β -phases.

Substances with γ_1 -structure:

Made from NaNiO_2 during oxidizing hydrolysis with hypobromide in a strong alkali or sodium solution (2.1).

Exceptions: from watery β -nickel (II) hydroxide and oxidation with hypobromide in strong alkali or sodium solution (2.3.1).

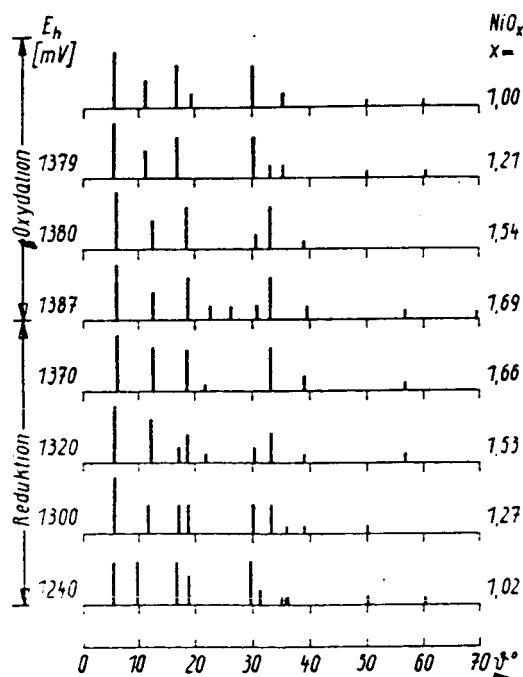


Fig. 6: Electro-static oxidation and reduction (reaction $\alpha - \gamma$)

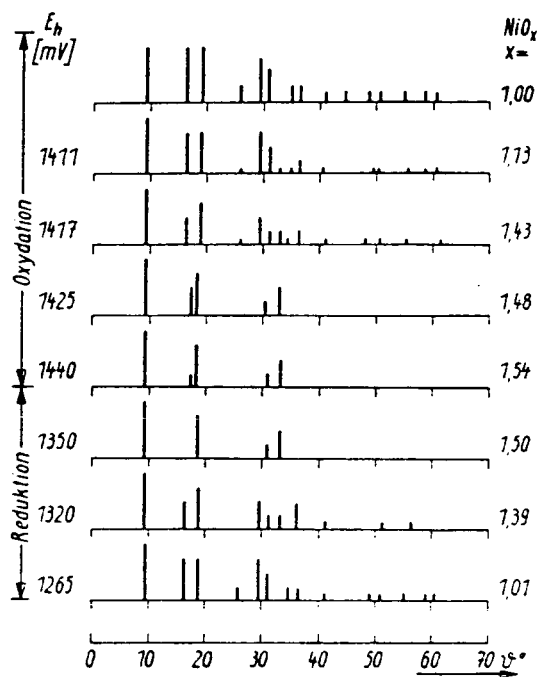


Fig. 7: Electro-static oxidation and reduction (reaction $\beta - \beta$)

Substances with γ_2 -structure:

Made from α -nickel hydroxide by electro-chemical oxidation or with hypobromide in weak alkali or sodium solution (2.4.1; 2.3.3).

Made from β -nickel (II) hydroxide by electro-chemical oxidation or with hypobromide in concentrated alkali or sodium solution (2.4.2; 2.3.1).

Made from salts of nickel solution with hypobromide in the presence of alkali or sodium solution (2.2.).

Made from β -nickel (III) hydroxide with hypobromide in concentrated alkali or sodium solution (2.3.1).

Substances with β -structure:

Made from β -nickel (II) hydroxide either electro-chemically or chemically in 0.1 n alkali or sodium solution (2.3.2; 2.4.3).

Made from lithium, rubidium or cesium-hydroxide solution or with the addition of sodium solution (2.2).

3. Chemical reduction of the γ -compounds

100 ml of watery hydrazine solution, with staggered concentration, is poured over 1 g of finely mortared substance of the γ_1 -phase and shaken. The reduced substance is left to work for 2-90 hours. The color changes from dark-grey via olive to light-green. The reduced product is cleansed of alkali and bromide with ice water and dried in a vacuum over P_4O_{10} . The Debye-diagram and analytically determined oxidation values are shown in Fig. 8.

The initial compound consists of $NiO_{1.80} \times 0.53 H_2O \times 0.13 K_2O$ and has a γ_1 structure. The reduction produces a compound of $NiO \times 1.32 H_2O$ which corresponds to the (II) structure of $Ni(OH)_2 \times 0.32 H_2O$. The reduction is heterogeneous. The first x-ray graphic indication of the reduced phase occurs at an oxidation value of between $NiO_{1.53}$.

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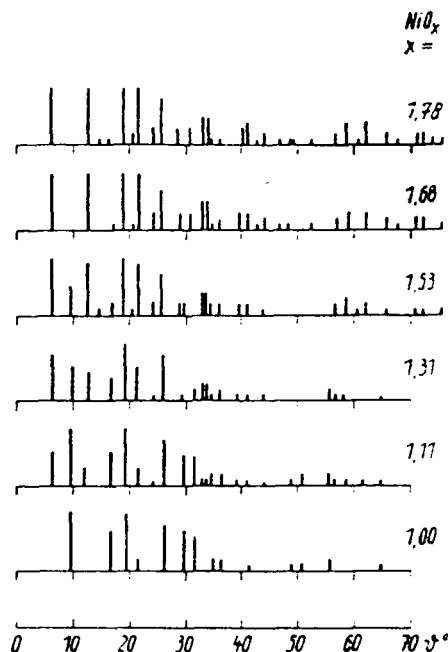


Fig. 8: Chemical reduction of a substance from y_1 -phase to β -nickel (II) hydroxide.

The y_2 -compounds also produce, by reduction with hydrogen peroxide in alkali solution, β -nickel (II) hydroxide. On the other hand, the y_2 compound is reduced to \mathcal{C} -nickel hydroxide in a solution of 1 ml perhydrol in 50 ml of water.

The \mathcal{C} -nickel hydroxide so obtained clearly distinguished itself from the freshly settled preparations (1) obtained from solutions of salts of nickel. Substances obtained from the reductions show, aside from base and prism-reflexes, pyramid reflexes also. These same can be noted with preparations aged in water (Table 5).

Phase	1 Hexagonale Aufstellung			3 Monokline Aufstellung			2 Raumgruppe	4 Zellvolumen Λ^3	Röntgenographische Dichte g/cm^3	Formeleinheiten pro Zelle (n)
	a	c	2 Raumgruppe	a	b	c				
β -Ni(OH) ₂	3,12	4,00	P 3 m1					38,78	3,97	1
α -3 Ni(OH) ₂ · 2 H ₂ O	5,34 = 3,09 $\sqrt{3}$	7,50	P 3 1 m	5,34	9,25	7,5		hex 185,2 mkl 370,4	2,82	1
β -NiOOH	2,81	9,53	P 3 1 c					65,0	4,68	2
γ -Phase [4 NiO ₂ · 2 NiOOH] · (2 H ₂ O · 2 OH · 2 Na)	4,90	0,96	P 3 1 m	4,90	8,49	6,96		mkl 290	3,79	1
γ -Phase [4 NiO ₂ · 2 NiOOH] · (2 H ₂ O · 2 OH · 2 Na)	2,83	21,0	R 3 m	4,00	8,49	7,17		mkl 291	3,78	1
NaNiO ₂ ¹⁰⁾				5,33	2,86	5,59		70,8	4,74	2

¹⁰⁾ D. DYER, B. S. BORTE u. G. P. SMITH, J. Amer. chem. Soc. 76, 1499 (1954).

Table 4: Grid constants of the described phases

1) Hexagonal arrangement 2) space group 3) monoclinic arrangement
4) cell volume 5) density of x-ray graphics 6) formula unit per cell

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4. Summary of the x-ray data

X-ray photos were made according to Debye-Scherrer with a Mueller device Mikro 111, CuK α radiation (30 KV, 26 mA), average exposure time 20 minutes, chamber diameter 57.3 mm and 114.6 mm.

4.1 β -Ni(OH) $_2$

For x-ray diagrams refer to ASTM index No. 14-117.

θ Cu	$10^3/d^2$	(h k l) _{hex}	(h k l) _{mon}	J
5,8	17	0 0 1	0 0 1	10
11,9	71	0 0 2	0 0 2	6
16,8	141	1 1 0	1 3 0; 2 0 0	8
17,6	154 ⁺)	1 1 1	1 3 1; 2 0 1	8
19,5	187	2 0 0	2 2 0; 0 4 0	5
20,6	209 ⁺)	1 1 2	1 3 2; 2 0 2	8
24,2	283	0 0 4	0 0 4	1
29,8	416	3 0 0	3 3 0; 0 6 0	7
30,5	434 ⁺)	3 0 1	3 3 1; 0 6 1	0,5
32,0	473 ⁺)	3 0 2	3 3 2; 0 6 2	0,5
34,6	540	2 2 0	2 6 0; 4 0 0	4
35,4	565 ⁺)	2 2 1	2 6 1; 4 0 1	1
49,6	980	4 1 0	4 6 0; 5 7 0; 1 9 0	2
59,5	1250	3 3 0	3 9 0; 6 0 0	2

4.2 α -3 Ni(OH) $_2$ x H $_2$ O

Table 5

Recorded x-ray data and their identification

⁺) These reflexes were only noted in aged and other preparations where a transformation had been carried out.

θ Cu	$10^3/d^2$	h k l	J
4,65	11*	0 0 1	5
9,35	44	0 0 2	10
14,00	99*	0 0 3	1
17,0	144 ⁺		(1)
18,45	169	1 0 0	7
24,0	279*	0 0 5	1
31,0	447 ⁺		(1)
33,2	503	1 1 0	7
39,2	672	2 0 0	0,5
56,3	1156	2 1 0	0,5

4.3 β -NiOOH

Table 6

Recorded x-ray data and their identification

These x-ray data represent average values of various preparations. The lines marked with a (+) were often found but cannot be identified with this system. The lines marked with (*) were not found in any preparations. If one ignores these, an identification as per $C = 4.76 \text{ \AA}$, is also possible.

θ Cu	$10^3/d^2$	(h k l) _{hex}	(h k l) _{mon}	J
6,26	20	0 0 3	0 0 1	10
12,70	81	0 0 6	0 0 2	10
18,55	171	1 0 1	1 3 0; 2 0 1	6
19,00	179	0 1 2	1 3 1; 2 0 0	8
20,46	206	1 0 4	2 0 2; 1 3 $\bar{1}$	4
21,30	223	0 1 5	1 3 2; 2 0 $\bar{1}$	9
23,85	276	1 0 7	2 0 3; 1 3 $\bar{2}$	6
25,45	311	0 1 8	1 3 3; 2 0 $\bar{2}$	8
26,05	325	0'0'12	0 0 4	4
28,75	390	1'0'10	2 0 4; 1 3 $\bar{3}$	6
30,70	439	0'1'11	1 3 4; 2 0 $\bar{3}$	6
33,10	503	0'0'15; 1 1 0	3 3 1; 0 6 0; 0 0 5	8
33,80	521	1 1 3	3 3 2; 3 3 0; 0 6 1	8
34,60	540	1'0'13	2 0 5; 1 3 $\bar{4}$	4
35,95	581	1 1 6	3 3 3; 3 3 $\bar{1}$; 0 6 2	6
36,70	602	0'1'14	1 3 5; 2 0 $\bar{4}$	2
39,35	677	2 0 2	4 0 2; 2 6 0	6
40,35	706	0 2 4	2 6 2; 4 0 0	2
40,90	723	2 0 5	4 0 3; 2 6 $\bar{1}$	6
41,35	735	0'0'18	0 0 6	2
42,85	779	0 2 7	2 6 3; 4 0 $\bar{1}$	4
43,95	812	2 0 8	4 0 4; 2 6 $\bar{2}$	6
44,40	826	1'1'12	3 3 5; 3 3 3	2
46,40	884	0'2'10	2 6 4; 4 0 $\bar{2}$	4
48,40	943	2'0'11	4 0 5; 2 6 $\bar{3}$	4
49,50	975	1'0'19	2 0 7; 1 3 $\bar{6}$	2
50,00	989	0'0'21	0 0 7	2
50,60	1006	1'1'15	3 3 6; 3 3 $\bar{4}$	4
52,05	1048	0'1'20	1 3 7; 2 0 $\bar{6}$	4
54,40	1114	2'0'14	4 0 6; 2 6 $\bar{4}$	2
55,75	1169	2 1 1	5 3 2; 4 6 1	2
56,90	1180	1 2 2	4 6 2; 5 3 1; 1 9 1	4
57,85	1208	2 1 4	5 3 3; 4 6 0; 1 9 $\bar{1}$	2
58,70	1231	1'1'18; 1 2 5	4 6 3; 5 3 0; 3 3 7; 3 3 $\bar{5}$; 1 9 2	7
59,30	1246	0'2'16	2 6 6; 4 0 $\bar{3}$	2
60,80	1280	2 1 7	5 3 4; 4 6 $\bar{1}$; 1 9 $\bar{2}$	4
61,10	1291	0'0'24	0 0 8	2
62,0	1315	1 2 8	4 6 4; 5 3 $\bar{1}$	2
63,40	1348	2'0'17	4 0 7; 2 6 $\bar{5}$	6
65,50	1396	0'1'23; 2'1'10	5 3 5; 4 6 2; 1 3 8; 2 0 $\bar{7}$	5
67,65	1442	1'2'11	4 6 5; 5 3 $\bar{2}$; 1 9 4	5
69,65	1482	0'2'19	2 6 7; 4 0 $\bar{5}$	4
70,90	1505	1'1'21	3 3 8; 3 3 $\bar{6}$	4
71,95	1524	3 0 3	6 0 3; 3 9 0	6
73,45	1549	2'1'13	5 3 6; 4 6 $\bar{3}$; 1 9 $\bar{1}$	2
75,90	1585	0 3 6; 2'0'20	3 9 3; 6 0 0; 4 0 $\bar{8}$; 2 6 $\bar{6}$	4

4.4 γ_1 -phase: $(4 \text{ NiO}_2 \times 2 \text{ NiOOH}) \times (2 \text{ H}_2\text{O} \times 2 \text{ OH}^- \times 2 \text{ Na}^+)$

Table 7

Recorded x-ray data and their identification

θ Cu	$10^3/d^2$	(h k l) _{hex}	(h k l) _{mon}	J
6,26	20	001	001	10
12,7	81	002	002	8
18,5	170	110	130; 200	10
21,4	224	200	220; 040	3
26,0	324	004	004	1
33,1	503	300	330; 060	8
39,2	672	220	260; 400	3
56,9	1180	410	190; 460; 530	2
71,9	1523	330	390; 600	2

4.5 y_2 -phase: $(4\text{NiO}_2 \times 2 \text{NiOOH}) \times (2 \text{H}_2\text{O} \times 2 \text{OH}^- \times 2 \text{Na}^+)$

Table 8

Recorded x-ray data and their identification

5. Discussion

The three production methods described lead to three substances which can be considered as pure phases. Two types can be distinguished.

1. β -type:

The oxidation condition of nickel is not very much above the $\text{NiO}_{1.5}$ level. The substances are free of sodium and potassium.

2. γ -type

The oxidation condition of nickel is always above $\text{NiO}_{1.5}$. These compounds have structurally integrated alkali which cannot be washed away. Two γ -phases are found which differ only in the size of the monoclinic angle.

These compounds can be described as grid levels from a crystallographic point of view.

The one level (main level) consists of a double layer of hexagonal, densely packed oxygen or hydroxide ions. The octagon gaps are occupied by nickel ions.

The other layer (intermediate layer) contains a simple hexagonal packing of oxygen or hydroxide ions, water and alkali ions or vacant grid spots in a changing ratio of quantities.

Only alkali ions of sodium or potassium are built into this

intermediate layer since the size difference between these ions and the oxygen is sufficiently small.

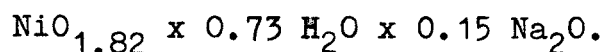
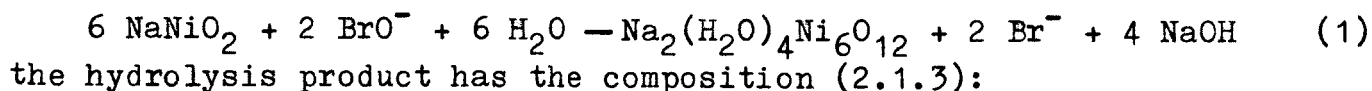
ρ -type compounds consist solely of main layers. The grid constant c_0 amounts to 4.6 Å to 4.7 Å, or multiples thereof, depending on the oxidation condition of the nickel.

α and γ -type compounds each have a main layer alternating with an intermediate layer placed on top of each other. The grid constant is about 7 Å.

The γ_1 -phase

An oxidizing hydrolysis of hypobromide crystals produces single crystals of NaNiO_2 which can be studied with the usual single crystal x-ray method. This allows one to draw conclusions of a topo-chemical reaction course and an internal connection of crystal structures.

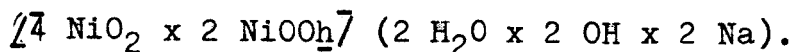
Based on the equations of reaction:



The reaction is to be understood as a substitution of sodium in the niccolate. The sodium niccolate NaNiO_2 crystallizes monoclinically in the space group C2/m . This is a grid layer with slightly deformed spherical packing of oxygen ions, the octagon gap of which accommodates sodium ions so that oxygen and sodium ions roughly form a cubic, dense, spherical packing (Dyer, Broie and Smith) (10).

The compound specified in (1) is obtained when two thirds of sodium ions are replaced by water molec. and when a three-valency nickel quantity equivalent to the sodium is oxidized to four-valency nickel. The reaction product is the compound γ_1 , and possesses the highest oxidation value (represented by $\text{NiO}_{1.83}$) observed by us.

We offer the following formulation for the structure of the γ_1 -phase:



The square parenthesis is meant to represent the main layer, the curved one the intermediate layer.

An elementary cell which accommodates the structure as stated in equation (I) contains six grid locations in the intermediate layer which can be occupied by ions or molecules the size of oxygen ions. Structure (I) is complete with two molecules of water, two hydroxide groups and two sodium ions.

The bonding of the alkali ions in the substances with the y_1 -structure may be due to the higher valency-nickel.

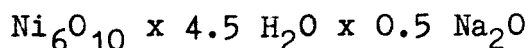
Other alkali or alkaline earth of similar size, e.g. K^+ or Ba^{++} can be accommodated instead of the sodium. Integrating the smaller Li^+ ions does not produce the same structure. We have not yet been able to integrate the larger Rb^+ and Cs^+ ions.

The monoclinic character of phase y_1 products were confirmed by single-crystal pictures. The layer distance in the (001)-direction amounts to 6.97 Å (compare 4.4).

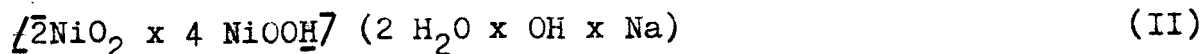
Debyeograms of such products - without the very weak superstructure lines - can also be identified with a sub-cell ($b = 2.83\text{Å}$) which has only one third of the structure weight. Single-crystal pictures show, however, that due to a superstructure - which will be dealt with in a later publication - the elementary cell must be assumed to be larger than stated in 4.4.

We wish to recall here a formal, genetic relationship of well-known structure data. Since the sub-cell ($a = 4.90$; $b = 2.83\text{ Å}$) is subject to the relationship $a = b\sqrt{3}$ and $\cos\beta = \frac{a}{3c}$ one can select a pseudo-rhombohedral arrangement of $a = 2.83$; $b = 21.0\text{ Å}$ which corresponds to the y -phase of Glemser and Einerhand (3) of $a = 2.83$ and $c = 20.9\text{ Å}$.

Oxidizing hydrolysis hypobromide in weak solutions ($c < 1\text{ n}$) also produces compounds of the y_1 -phase (compare 2.1). Alkali contents and oxidation values of such hydrolysis products are, however, smaller. They are of the structure



which corresponds to the arrangement of

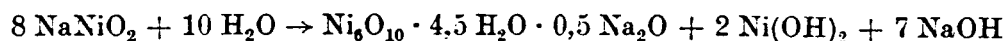


with two unoccupied grid locations.

The characterized substances of (I) and (II) cannot be distinguished by radiography. Both produce good Debyeograms of identical line sequences and identical intensities.

Substances (I) and (II) represent the limits of the y_1 -phase composition between which the oxidation value and alkali contents may fluctuate. By using concentrated lyes on the components of substance (II) the alkali contents can be increased without changing the oxidation value.

Hydrolysis of the sodium niccolate carried out without simultaneous oxidation results in $\text{NiO}_{1.5} \times 0.81 \text{ H}_2\text{O} \times 0.063 \text{ Na}_2\text{O}$ (2.1.2). Since radiography of the reaction products shows β -nickel (II) hydroxide and the y_1 phase, one can assume a disproportional reaction as follows:

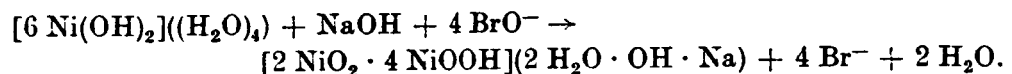


Equation (2) p. 16

The oxidized portion corresponds to equation (II) since it is a reaction in a weak solution. With respect to alkali contents also compare Dyer, Borie and Smith (10).

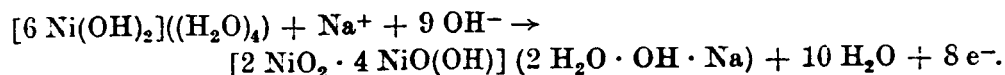
The y_2 -phase

Starting with α -nickel (II) hydroxide one can produce compounds with y_2 -structure via a topochemical reaction. The oxidation with hypobromide can be formulated as follows (2.3.3):



Equation (3) p. 16

If α -hydroxide is electro-chemically oxidized then the reaction is as follows:



Equation (4) P. 17

This reaction is based on anodic treatment of thin layers of α -nickel hydroxide by galvanimetric (2.4.1) or electro-static (2.4.3) methods. This reaction also frequently produces substances with a higher oxidation value ($\text{NiO}_{1.75}$ or $\frac{1}{3} \text{NiO}_2 \times 3 \text{NiO}(\text{OH})_7$).

Oxidation takes place within a narrow voltage range of about 10mV. Initial and final products are close together with respect to average oxidation values (Fig. 4 and 6). The reactions proceed heterogenously.

The reaction can be reversed by loading the cathode (Fig. 6). This reversal also takes place within a small voltage range which, however, compared to oxidation, shifts towards lower values.

The oxidation products, like the α -nickel hydroxide, can be identified in a hexagonal manner (compare 4.5). Since these products do not correspond to substances produced from NaNiO_2 they are named the y_2 -phase.

One would assume similar conditions for the y_2 -nickel hydroxide as Feitknecht and Collet (11) have observed on basic nickel nitrates which they interpreted as a single-dimension, marginal arrangement in direction (c). The absence of (hkl) reflexes is characteristic of this configuration.

Aging or chemical transformation of these phases often produces a better orientation of layers which is confirmed by the appearance of weak (hkl) reflexes.

An example is the partial elimination of a marginal configuration during reduction of a y_2 -phase to α nickel hydroxide as described in Gl. (3). The α -nickel hydroxide so obtained also shows weak (hkl) reflexes (Table 4).

Apart from the hexagonal configuration with three nickel atoms each in the cell, one can also select an orthohexagonal arrangement for both the y_1 -phase and the y_2 -phase (Table 4). Here the cell has six nickel atoms like the y_1 -phase. They only differ

in their monoclinic angle. Due to the hexagonal configuration it must be 90° for the y_2 -phase.

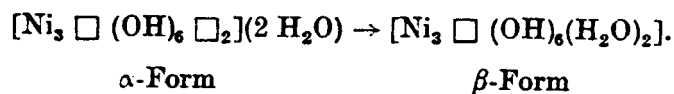
Measuring line-profiles of suitable reflexes did not show any deviation of the monoclinic angle of 90° . The accuracy is not very great since y_2 and \mathcal{C} phases could only be produced in powder form.

The β -Phase

Substances of the β -type, i.e. without intermediate layers, also submit to various, characteristic reactions.

β -nickel (II) hydroxide can be produced from \mathcal{C} -nickel (II) hydroxide by shaking it in concentrated lyes or by boiling in water. The \mathcal{C} hydroxide loses water from the intermediate layer. Formation of β -hydroxide can be recognized by shortening of the grid constant c_0 from 7.5 \AA (\mathcal{C} -phase) to 4.6 \AA (β -phase). The transformation occurs in an monotropic and heterogeneous manner.

The resulting β -nickel (II) hydroxide has a high water content which corresponds to the \mathcal{C} -nickel (II) hydroxide with the composition $3\text{Ni}(\text{OH})_2 \times 2 \text{H}_2\text{O}$. Assuming marginal locations in the main layer the transformation of \mathcal{C} -nickel (II) hydroxide into β -nickel (II) hydroxide can be described as follows:



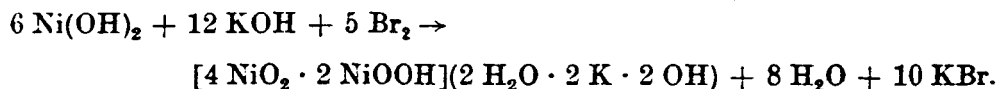
Equation (5) P. 18

The water molecules of the intermediate layer transfer to the vacant locations of the main layer and only the octagon gaps of the main layer, not occupied by nickel ions, remain vacant.

β -nickel (II) hydroxide produces, depending on type and concentration of the lye, the following oxidation products:

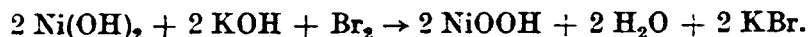
An intermediate layer is formed during the swelling process when using concentrated (9n) bromic sodium or potash lye producing compounds with y -phases usually together with the y_2 -phase.

The intermediate layer of such compounds contain sodium and potash ions:



Equation (6) P. 18

Oxidation in weak (0.1 n) sodium or potash lye transforms β -nickel (II) hydroxide to β -nickel (III) hydroxide:



Equation (7) P. 18

Oxidation in bromic lithiumhydromid solutions produces lithium-containing reaction products with β -structure. It seems likely that the small Li^+ ion is integrated into the octagon gaps of the oxygen or main layers and, in order to compensate the charge, the neighboring Ni-atoms assume a valency of four. This would also account for the unusual oxidation value of $\beta\text{-NiO}_{1.5}$ (Table 3) within the β -structure.

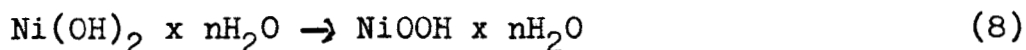
Electro-static and galvanometric oxidation of β -nickel (II) hydroxide (in weak solutions) produces β -nickel (III) hydroxide. The oxidation of α -nickel hydroxide also occurs within a small voltage range which, however, is shifted by about 40 mV towards positive voltage (compare Fig. 5 and 7). Partially oxidized substances contain the reflexes of the reduced and oxidized phase in parallel, i.e. the oxidation takes a heterogeneous course.

Radiography of such β -nickel (III) hydroxide shows superstructure lines which can be explained by a doubling of the c-axis to 9.53 Å since the odd arrangements in the x-ray diagrams occur in addition to the enlarged grid plane distances. We have always noted that the hexagonal configuration of present (hkl)-reflexes of β -nickel (II) hydroxide disappear during oxidation but reappear during the electro-static reduction.

The doubling of the c-axis at oxidized nickel hydroxide can be understood to be analogous to the structure as described by Douglass (12).

This type of structure consists of main layers of brucite but the sequence of layers is not in the sense of a spherical packing. The oxygen atoms are instead arranged between the layers perpendicular to the (001)-level, in pairs on top of each other, so that a hydrogen bridge formation can be created between them. Such a model leads to a doubling of the single c-axis if the metal atoms in the octagon gaps are shaped like a hexagonal matrix as is the case with β -nickel (III) hydroxide. The necessary translation to create such a configuration of main layers, which initially will extend only over partial areas, would explain the disappearance of the (hkl)-reflexes.

It is easy to achieve oxidation of water containing nickel hydroxide. The water content remains practically unchanged during reaction (2.3.2):



Products free of water created by hydrothermal or aging processes are very difficult to oxidize. The water contained in hydroxide is obviously necessary for the oxidation. Aging, as often noted in nickel hydroxide electrodes, may be due to a loss of water bonded in the main layers (compare Milner and Thomas (2)).

Precipitation and oxidation of nickel hydroxides from nickel-nitrate solutions

As has been shown by Feitknecht and Collet (11) the precipitation of nickel hydroxides from nickel-nitrate solution produces basic nitrates of varying composition. The product IIIa indicated offers an especially extended range of products. It is composed of $1 \text{ Ni(NO}_3)_2 \times 5 \text{ Ni(OH)}_2 \times 6-7 \text{ H}_2\text{O}$ which turns into a more defined product III after aging. Its radiogram has been identified as: hexagonal $a = 3.10 \pm 0.01 \text{ \AA}$ and $c = 6.95 \pm 0.05 \text{ \AA}$.

In our opinion this substance could have the formula $[\text{6 Ni(OH)}_2] \times (2 \text{ H}_2\text{O} \times 2 \text{ H}_3\text{O}^+ \times 2 \text{ NO}_3^-)$ and its structure would correspond to the α -nickel hydroxide: $[\text{6 Ni(OH)}_2] / (4 \text{ H}_2\text{O} \times 2 \square)$.

This would mean that the basic nickel (II) hydroxide was isotypical with the α -nickel hydroxide found by us. It has an already existing intermediate layer.

If precipitation takes place in ample potassium or sodium lye, in the presence of hypobromide, a γ_2 -compound results. The primary forming intermediate layer during precipitation is conserved and will be stabilized by potash or sodium ions and oxidation.

Precipitation and oxidation with hypobromide in solutions of lithium, rubidium and cesium as well as with peroxodisulfate does not stabilize the primary forming intermediate layer due to a lack of suitably sized alkali-ions and β -nickel (III) hydroxide is produced.

Magnetic-chemical studies

Oxidation of nickel (II) compounds can be done via two types of reactions:

1. Three-valency nickel is formed initially which is then oxidized to a valency of four.
2. Right from the beginning three or four valency nickel is produced.

For a further discussion of these two methods we will refer to magnetic measurements made by Labat (13):

Labat oxidized nickel (II) saline solutions with potassium lye and peroxodisulphate as well as with potassium lye and hypobromide or hypochloride. No radiography was made of these substances. One may conclude, however, from other Lavat test series and our own results that oxidation with peroxodisulphate produced β -nickel (II) hydroxide and oxidation with hypoalogenites created the γ -phase.

Labat's experimental results can be represented by the following equation for oxidation with peroxodisulphate in which n is the oxidation value and x the susceptibility:

$$x_{\text{ber.}}^{25} \times 10^6 = 4706 - 6817 (n - 1).$$

The transition from two-valency to three-valency nickel can be expressed theoretically as follows:

$$x_{\text{ber.}}^{25} \times 10^6 = 4720 - 6800 (n - 1).$$

Agreement of observed and calculated values correspond to Labat who has found a transition from two-valency nickel to three-valency nickel during oxidation with peroxodisulphate.

The situation is different for oxidation with hypochloride and hypobromide. The results of two test series carried out by Labat are represented by the following equation:

$$x_{\text{exp.}}^{25} \times 10^6 = 4712 - 5829 (n - 1).$$

Assuming that oxidation of two-valency nickel straight away produces three and four-valency nickel, then one obtains the following equation for the y-phase:

$$x_{\text{ber.}}^{25} \times 10^6 = 4720 - 5760 (n - 1).$$

Agreement in the last two equations shows that there existed an initial y-phase which forms fixed valency ratios up to $\text{NiO}_{1.67}$. Since the reaction is heterogeneous one obtains with increasing oxidation values, apart from the initial product $\text{Ni}(\text{OH})_2$, ever increasing portions of phase (II) $\frac{1}{2} \text{NiO}_2 \times 4 \text{NiO}(\text{OH}) \cdot 2 \text{H}_2\text{O}(\text{OH})\text{K}$. This statement differs from the conclusion given by Labat. The course of the reaction may differ depending on the oxidation medium used.

Further oxidation up to the value of $\text{NiO}_{1.75}$ shows that the two oxidation media (peroxosulphate and hypohalogenite) create reaction products with the same susceptibility value. According to Labat's calculations there should be, apart from small portions of bi-valent nickel of unchanged initial product, equal parts of three and four valency nickel for the oxidation value $\text{NiO}_{1.75}$.

Magnetic measurements of a substance produced by us from NaNiO_2 (2.1) with the oxidation value $\text{NiO}_{1.81}$ and y_1 -structure showed the ratio $\text{Ni}^{2+} : \text{Ni}^{3+} : \text{Ni}^{4+} = 0.03 : 0.30 : 0.66$. This number ratio corresponds exactly to the compound described under (I).

Conclusion

Evaluation of the extensive, experimental material contained in this article has led us to the model introduced here. Other tests to study capacity and discharge of the phases with respect to the nickeloxide electrode will be reported at a later stage.

Dipl.-Ing. K. Dehmelt and Dr. J. Witte carried out the basic experiments. However, these gentlemen were not involved in the final draft of this study. Drs. W. Dennstedt and W. Loeser gave detailed assistance in the final experimental work, the evaluation of results and in writing the manuscript. I would like to offer these gentlemen my heartfelt thanks. I am also grateful to Dr. G. Sterr who revised the radiographic part and Prof. W. Bronger (Muenster University) who carried out the magnetic measurements. I would also like to thank the Board of Directors of VARTA AG who permitted publication of this article.

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16. Abstract ↓ 120525s Nickel hydroxide electrodes. II. Oxidation products of nickel(II) hydroxides. Bode, Hans; Dehmelt, Klaus; Witte, Josef (VARTA Forschungs- und Entwicklungszentrum, Kelkheim, Ger.). <i>Z. Anorg. Allg. Chem.</i> 1969, 366(1-2), 1-21 (Ger). Pure phases of some oxidized Ni oxides were prep'd. galvanimetrically with the Ni(II) hydroxide electrode of an alk. battery (phase, compn., geometry, space group, <i>a</i> , <i>b</i> , <i>c</i> (Å.), β , <i>d</i> , <i>Z</i> given): α -phase, $3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, hexagonal, $P\bar{3}1m$, 5.34, —, 7.50, —, 2.82, 1; α , $3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, monoclinic, $C2/m$, 5.34, 9.25, 7.5, 90° , 2.82, 2; γ_2 , $[\text{4NiO}_2 \cdot 2\text{NiO}_2\text{H}](\cdot 2\text{H}_2\text{O} \cdot 2\text{OH} \cdot 2\text{Na})$, hexagonal, $P\bar{3}1m$, 4.90, —, 6.96, —, 3.79, 1; γ_3 , $[\text{4NiO}_2 \cdot 2\text{NiO}_2\text{H}](\cdot 2\text{H}_2\text{O} \cdot 2\text{OH} \cdot 2\text{Na})$, monoclinic, $C2/m$, 4.90, 8.49, 6.96, 90° , 3.79, 1; γ_1 , $[\text{4NiO}_2 \cdot 2\text{NiO}_2\text{H}](\cdot 2\text{H}_2\text{O} \cdot 2\text{OH} \cdot 2\text{Na})$, hexagonal, $R\bar{3}m$, 2.83, —, 21.0, —, 3.78, 1; γ_1 , $[\text{4NiO}_2 \cdot 2\text{NiO}_2\text{H}](\cdot 2\text{H}_2\text{O} \cdot 2\text{OH} \cdot 2\text{Na})$, monoclinic, $C2/m$, 4.90, 8.49, 7.17, 103.1° , 3.79, 1. The phases were characterized by susceptibility measurements. CJJG			
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